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The Determination of Methoxyl in the Presence of Carbohydrates 1/

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In the A.O.A.C. (1) method for determining, "Methoxyl Group", there is the statement, "Applicable to lignin and quaiacol only". The extension of this method to material containing a large percentage of carbohydrates would make this analysis more useful.

Methoxyl determinations on some pure naturally occurring carbohydrates give a"Methoxyl" titer. Tests were made with α-cellulose, Bureau of Standards glucose, and pectin. Five successive runs with 90 minutes distillation were made with each material. The results are shown in Table 1.

Table 1. Methoxyl values obtained from carbohydrates during successive distillations.

Period	α-cellulose Mg.	Bureau of Standards glucose Mg.	Pectin Mg.	Blank Mg.
1st 90 min.	.452	.504		.042
2nd 90 min.	.442	.520	.343	.018
3rd 90 min	.436	.559	.358	.010
4th 90 min.	.343	.598	.366	.013
5th 90 min.	.452	.691	.384	.039

In all these runs for a given material the successive values are fairly constant. This would indicate that a successive run can be used as a blank to correct for the effect of carbohydrates in a sample.

The strong reducing action of hydriodic acid on carbohydrates liberates large amounts of I_2 and water. Thus 10 equivalents of iodine may be released for each equivalent of glucose. The water that is formed dilutes the hydriodic acid and increases the vapor pressure of the acid. This increases the iodine carrying capacity of the vapors. The problem, therefore, is to keep the iodine from distilling over with the methyl iodide.

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The method proposed for methoxyl in the presence of carbohydrates, and incorporating modifications of the apparatus is as follows: The apparatus specified by Clark (2) was modified to make it more convenient to manipulate. The tube through which CO_2 or N_2 bubbles is arranged so that the gas passes through the hydriodic acid in the distillation flask. The scrubbing trap consists of a standard taper joint in which the female portion is fitted with a flask of about 3 ml. capacity for the 1% starch solution. The trap is convenient to load and is self-sealing. The delivery tube has a fritted glass bubbling device which can be connected with a standard taper joint. The reagents used are those specified in the A.O.A.C. method except phenol and mercury are not needed. A sample of about 0.5 grams is accurately weighed and transferred to the 50 ml. boiling flask. 15 ml. hydriodic acid is added. The receiver is filled with the acetic acid-potassium acetate-bromine solution and is connected to the delivery tube. The trap is filled with 1% starch solution. Carbon dioxide or nitrogen is bubbled through the hydriodic acid at the rate of two bubbles per second. The flask is heated on a steam bath for 1 1/2 hours. This time is sufficient to effect quantitative recovery of vanillin in the presence of 0.5 g α-cellulose. In the case of material containing carbohydrates the distillation is run for 90 minutes. A fresh receiver is then connected, and the distillation continued for an additional 90 minutes. The second distillation serves as blank. The contents of each receiver is washed into a 125 ml. flask which contains 5 ml. of 25% sodium acetate. The bromine is discharged with formic acid and the last trace of bromine is blown out with air. 5 ml. of 10% sulfuric acid is added and 0.5 gram potassium iodide is added. The liberated iodine is titrated against .05 N sodium thiosulfate. The calculations are the same as the A.O.A.C. method that is:

$$\frac{\text{(titer-blank) N X 5.17 X 100}}{\text{Sample weight in mg.}} = \% \text{ methoxyl}$$

REFERENCES

1. Association of Official Agricultural Chemists. Official Methods of Analysis of the Association of Official Agricultural Chemists. Washington 4, D. C. 8th ed. 1955.

2. Clark, E. P. The Vieböck and Schwappach Method for the Determination of Methoxyl and Ethoxyl Groups. J. Assoc. Offic. Agr. Chemists, 15: 136, 1932.